it was pointed out that the properties of the xylenes, like those of the octanes, are entirely in accord with the theory of atomic compressibility.

Ethyl benzene is not very different from *m*-xylene as regards its physical properties, but the correspondence between them, as regards these properties, is not so close as between the individuals of any pair of the three xylenes. This would indeed be expected, because of the difference in structure.

"Total surface energy" is seen to vary very little with changing temperature.

We are glad to acknowledge the assistance of a grant from the Carnegie Institution of Washington.

Summary

This paper recounts experimental work performed in 1910, which has awaited publication until more exact knowledge of the problem of medium-sized capillary tubes had been secured. The method consisted in the measurement of differences of capillary rise in two narrow tubes of different diameters. Now that the means for calculating the correction to the rise in the wider of these tubes is certain, this method becomes a very convenient one for the purpose, possessing many advantages. The tube was standardized by means of pure water. With it the surface tension of water, three isomeric octanes, *o*-, *m*- and *p*-xylene and ethyl benzene were determined, each at three temperatures. Equations are given for the calculation of the surface tension at any intervening temperature. The total surface energies are recorded; they change but slightly with changing temperature. The results are essentially in accord with the theory of atomic compressibility.

Cambridge 38, Massachusetts

NOTES

Density and Hydration in Gelatin Sols.—In a recent article, Svedberg and Stein[1] determined "*d*," the change in density when 5 g. of gelatin was suspended in 100 cc. of various solutions. The following quotation gives their method of calculation.

> "The volume of the pycnometer was determined in the usual way. The density difference, *d*, was arrived at quite directly: the difference in weight between the pycnometer plus the gelatin sol and the pycnometer plus the pure solvent was divided by the volume of the pycnometer. A concrete example taken from the results will make the statement clearer. For 5% gelatin solution in *N* hydrochloric acid we find,

$$\begin{array}{lll} N\,\text{HCl solution} & +\ \text{pyc.} & = 50.8212\ \text{g.} \\ N\,\text{HCl} & +\ \text{pyc.} & = \underline{50.4740} \\ \quad\text{Diff.} & & = 0.3472 \end{array} \qquad \frac{0.3472}{\text{vol. of pyc. } (27.17565)} = d = 0.012776.\text{''}$$

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[1] Svedberg and Stein, This Journal, **45**, 2613 (1923).

The changes in density are ascribed to "the formation of a shell of highly compressed water around the gelatin particle." With strong solutions the change of density was less than with weak solutions. This is ascribed to a contest set up between the gelatin particles and the solute for the possession of the water. Ethyl alcohol, and methyl alcohol gave anomalous results in that "d," the increase in density, increased with increasing concentration of these solutes. "Apparently their presence encourages the hydration of the gelatin."

The conclusions are in error and the form in which the data are arranged is misleading because the method of calculating change in density does not take into account the fact that for each different solution the change in density is calculated from a different basic density. The results are really due solely or almost solely to the fact that a nearly constant volume of gelatin displaces its own volume of solution in the pycnometer. The gelatin is denser than any of the liquids; hence, there is always an increase in gross weight when gelatin is added. That increase in weight is equal to the weight of the gelatin diminished by the weight of the equal volume of solution displaced; the less dense the solution, the greater this difference. Hence, the alcohol solutions show a greater increase in density than the pure water.

If there is no condensed shell of water, the weight of 1 cc. of a gelatin sol can be expressed by the equation

$$\sigma v + \rho(1-v) = D = \rho + d \qquad (1)$$

where σ is the density of gelatin; v, the volume of gelatin in 1 cc. of sol; ρ, the density of the dispersing medium; D, the density of the sol; and d the increase in density as found by Svedberg and Stein.

Using pure water at 37.2°, $d = 0.01443$, $\rho = 0.9933$, $D = 1.00773$; σ and v can be calculated by a series of approximations.

Assume that $\rho = 1.4$. Then 5 g. of gelatin occupies $5 \div 1.4 = 3.571$ cc., and 100 cc. of solution + 5 g. of gelatin become 103.571 cc. Each cubic centimeter contains $5 \div 103.571 = 0.04827$ g. of gelatin. This displaces $0.04827 - 0.01443 = 0.03384$ g. of water. 0.03384 g. of water occupies $0.03384 + 0.9933 = 0.03407$ cc. Then $\sigma = 0.04827 \div 0.03407 = 1.417$.

If a second calculation is made beginning with $\sigma = 1.417$, the correct value is found to be 1.417.

Equation 1 may be put in the form, $d = v(\sigma - \rho)$, and d calculated on the assumption that no condensed shell of water forms; ρ is taken from the published tables of densities by interpolation. For 2 N H_2SO_4, $\rho = 1.0636$. Then $d = (1.417 - 1.0636)\ 0.03407 = 0.01203$; Svedberg and Stein's value is 0.01145. For 2 N ethyl alcohol, $\rho = 0.9874$; $d = (1.417 - 0.9874)\ 0.03407 = 0.01464$; Svedberg and Stein's value is 0.01514. The concentrations of the solutions they used were only approximate and a variation 0.001 in the interpolated densities of the solutions would give calculated values almost identical with the observed values.[2,3]

Contribution from the Chemistry Department F. E. Brown
Iowa State College
Ames, Iowa

Received November 16, 1923

A Receiving Apparatus for Practical Distillation at Low Pressures.—Anyone who may have had to carry out a fractional distillation at low pressures knows the difficulties encountered in overcoming leaks in the various forms of vacuum distillation receivers. To avoid all leaks and yet be able to perform a continuous fractional distillation, the apparatus as shown in the diagram was constructed and found to work satisfactorily.[1]

The whole apparatus was made of Pyrex glass. This allowed it to be heated whenever there was a possibility of fractions solidifying and blocking the funnel. The details of construction are shown in the figure and are as follows: two metal plates serve to hold the funnel in position and they are in turn supported by constrictions in the large tube; clamped to the funnel are two small pieces of iron rod held together at the ends by brass strips; the funnel with the fixtures turns on a glass bearing which rests in a small indentation. Pivoted in this manner, the funnel and connections swing about easily when a magnet is brought near to either one of the iron pieces.

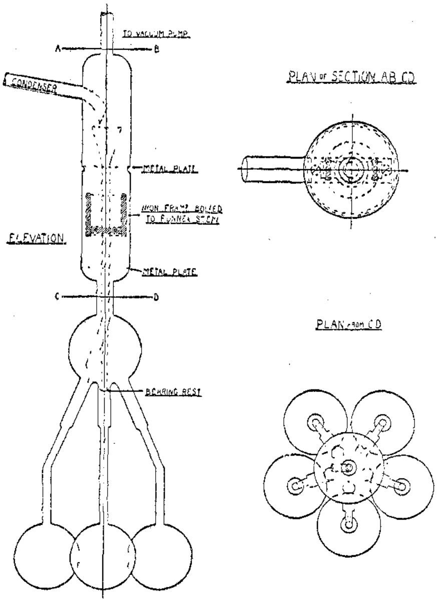

Fig. 1.

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[2] *Editor's Note.* Dr. Svedberg in a private communication to the Editor states that, in view of Mr. Brown's suggestions, he is now determining by means of a dilatometric method the corrections required to ascertain the actual volume changes. He has already found that there is a contraction attending the solution of gelatin in pure water, of about 50 cubic millimeters per 100 cc. This contraction becomes steadily less with increasing concentration of hydrochloric acid.

[3] The author has already commenced a determination of the partial molal volumes of gelatin and of water in various proportions by the methods described on pp. 33–41 of "Thermodynamics" by Lewis and Randall.

[1] A receiver similar to this has been described in the *Chem.-Ztg.*, **1902,** 337, and in Catalog No. 60 of the Kny-Scheerer Company.

Thus by means of a magnet, the lower end of the funnel may be brought directly over a number of outlet tubes sealed into the apparatus. Five of these outlets (only three are shown in the figure) have been found to be a convenient number. The outlet tubes are, in turn, sealed to flasks whose sizes are determined by the amounts of the various fractions. In some cases it may be found preferable to connect the outlet tubes to the flasks by means of ground glass joints with mercury seal.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BRITISH COLUMBIA
VANCOUVER
W. F. SEYER
RECEIVED DECEMBER 17, 1923

A Lecture Table Demonstration to Illustrate that the Conductivity of a Solution is Due to its Ions.—This demonstration visualizes the conductive property of the ions of an electrolyte and shows that as they form part of an undissociated compound or insoluble precipitate the concentration of the electrolyte is diminished with the consequent decrease in conductance.

The apparatus consists of a beaker containing platinum electrodes which are connected in series with an electric light bulb and an alternating current source. The electrolyte placed in the beaker is a 5% solution of barium hydroxide. As this is a moderately strong base, the light will burn brightly, showing the conductivity due to the barium and hydroxyl ions. While the solution is stirred, dil. sulfuric acid is added slowly from a buret. As the base becomes neutralized, the light gradually becomes dimmer. When just enough acid has been added to neutralize all of the base, the light goes out entirely indicating the absence of all ions. When, now, a slight excess of the acid is added, the current begins to pass again and the filament to glow due to the presence of hydrogen and sulfate ions. The neutralization is made more striking by the addition of phenolphthalein, which fades at the same time that the light goes out.

From a consideration of the equation, $Ba(OH)_2 + H_2SO_4 = 2H_2O + BaSO_4$, it is seen that this is a unique reaction in that both undissociated water and a very insoluble salt are formed, and at the neutral point the conductivity is at a minimum, as practically all ions are removed from the system. This also visualizes the principle upon which depends the determination of the concentration of an electrolyte by conductance measurements.

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OTTO O. WATTS
RECEIVED DECEMBER 31, 1923

The Action of Ammonium Hydroxide on Copper Ferrocyanide.—Treadwell and Hall[1] make the statement that copper ferrocyanide dis-

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[1] Treadwell and Hall, "Treatise on Analytical Chemistry," John Wiley and Sons, New York, **1916**, 4th ed., vol. 1, p. 220.

solves in ammonium hydroxide to give the intensely blue solution characteristic of cupri-ammonium ion. The writer has found, however, that when dilute ammonium hydroxide is slowly added to precipitated copper ferrocyanide, and the mixture shaken after each addition, the mahogany-brown precipitate is completely converted to a silky, dark brown solid, probably a substance of the formula $Cu_2Fe(CN)_6.4NH_3$.[2] This precipitate does not dissolve in concd. ammonium hydroxide, and is only slowly changed to copper sulfide when treated with hydrogen sulfide. Acetic acid, however, restores the copper ferrocyanide.

Scott[3] also states that the ferrocyanide of copper is soluble in ammonium hydroxide, and hence its presence must be avoided in the detection of traces of copper by the ferrocyanide method. When to two exceedingly dilute solutions of cupric sulfate, only one of which contained a trace of free ammonia, potassium ferrocyanide was added, the one without the trace of ammonia showed the usual characteristic deep red color, but the other developed a light brown color from which the silky, brown precipitate noted above settled on standing. These results could be duplicated as often as desired. They are to be interpreted as indicating that even the slightest trace of ammonia will seriously impair, if not completely obscure, the delicacy (1 part in 2,500,000) of the ferrocyanide test.

Contribution from
Columbia University
New York City
E. D. Crittenden

Received August 13, 1923

[Contribution from the Kent Chemical Laboratory of the University of Chicago and the Otho Sprague Memorial Institute]

FACTORS AFFECTING THE STABILITY OF MERCURIALS AND THE MERCURATION OF SUBSTITUTED PHENYLAMMONIUM SALTS

By Morris S. Kharasch and Lyman Chalkley, Jr.

Received August 30, 1923

It is a well established fact that amino and hydroxyl groups in a benzene ring enhance the ease of substitution of the *para* and *ortho* hydrogen atoms. We should expect, therefore, that any positive group,[1] *para* or *ortho* to an

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[2] Bunsen, *Pogg. Ann.*, **34**, 134 (1835). See also Messner, *Z. anorg. Chem.*, **8**, 393 (1895).

[3] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, **1918**, 2nd ed., p. 166.

[1] The term positive group is rather indefinite. There are various degrees of "positivity" of positive groups depending upon the position of the pair of electrons with respect to the carbon atom. The arrangement of positive groups in the order of their "positivity" will be given in a subsequent paper by one of us (Kh.) in conjunction with the heats of combustion of organic compounds.